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| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT This report explores the preparation of photovoltaic devices with enhanced light harvesting characteristics. In particular plastic hybrid photovoltaic devices based on electroactive polymer/inorganic components are studied. Significant advances were made in polymer-nanocrystal as well as polymer-titania photovoltaic devices through the development of novel polythiophenes that enhance both the interface and electronic communications between the polymer and the inorganic. | | | | | |
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1) Dendritic antennae and energy harvesting

We have demonstrated the concept of using dendrimers to array chromophores in an antenna configuration [1] capable of harvesting light and focusing the collected energy to a single point where it can be reprocessed as follows:

- (i) Transformation of light into light of a different wavelength, a concept that we have applied in the development of a UV to IR converter.
- (ii) Transformation of light into electricity for photovoltaic systems.
- (iii) Transformation of light into chemical energy for photocatalysis.

2) Dendritic antennae as coatings for classical Si based photovoltaics

In an early approach carried out in collaboration with Clay Mayberry and Paul Hausgen at Kirtland AFB, we explored the coating of standard Amorphous-Si (3-J) (699-885 nm) and the 3-junction GaInP2IGaAsIGe (650-1850nm) photocells with dendritic antennae designed to increase the absorption cross section of the cell to better match the solar spectrum. Unfortunately while the compounds we prepared are capable of absorbing additional light, the cell design is unsuitable for such an approach as light harvested/converted by the dendrimer is emitted in all directions and therefore cannot be used efficiently. As a result, the dendrimer coating effectively filters some of the light that would normally reach the cell surface and no increase in overall efficiency is observed.

A solution to this problem would involve a special cell design termed a "solar concentrator" (Figure 1) previously described by others [2] as a means of improving the efficiency of light harvesting for photocells. While technically feasible, such a design is costly and is not practical. As a result, this approach was abandoned.

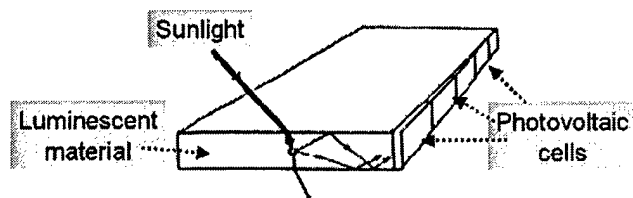


Figure 1: Design of a solar concentrator (adapted from reference 2)

3) Dendritic antennae and the Grätzel cell.

As an alternative to the dendrimer coated Si-based cells, we explored the use of dendritic antennae to improve the performance of Grätzel cells through an increase in the light absorption capability of the cell.

The Grätzel cell [3] consists of nanocrystalline TiO_2 film deposited onto the conducting glass electrode. Ruthenium dye is used to sensitize the wide bandgap TiO_2 semiconductor to the visible light (Figure 2, center panel). The regeneration of the oxidized dye is accomplished by iodine/triiodide redox electrolyte, which shuttles electrons from the Pt counter-electrode. Electrical load, connected to conducting glass electrode and to Pt counter-electrode, completes the circuit. The maximum IPCE is over 85 %, whereas power conversion efficiency is 10.4 %, making this cell comparable to several types of silicon-based photovoltaics. These high values are attributed to the almost 100 % efficiency of the electron injection from the excited Ru dye into TiO_2 , and to the very slow charge recombination.

Figure 2 shows the conceptual approach we used involving the attachment of a light-harvesting array of chromophores onto the Ruthenium dye, which is solely responsible for light absorption in the original cell. Figure 2(a) shows a close-up schematic representation of the standard configuration of the Grätzel cell with the Ru dye deposited onto the surface of the titanium dioxide semiconductor. Figure 2(b) shows a schematic of the overall cell with its sintered array of Ru-dye coated nanoparticulate titania surrounded by the liquid electrolyte. Figure 2(c) shows close-up schematic representation of the modified Grätzel cell we developed in which the Ruthenium dye has been

modified with additional chromophores to increase the portion of the solar spectrum that can be harvested by the cell.

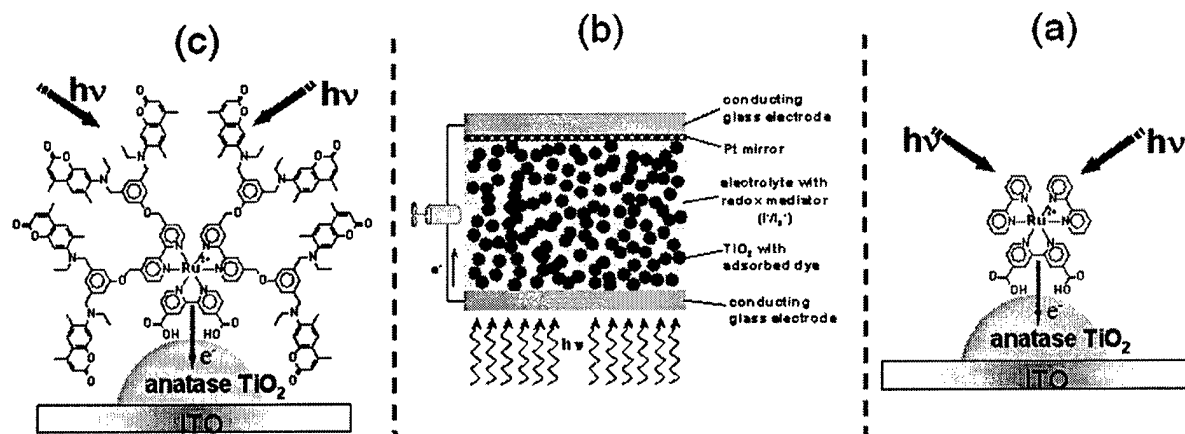


Figure 2. Conceptual design of a Grätzel cell with enhanced light-harvesting dendritic chromophores attached to the Ruthenium dye.

The chromophore chosen for this initial feasibility study was Fluorol 7GA since it absorbs light that is not normally harvested by the standard Ru-chromophore. We therefore designed and synthesized a new Ru dye with short dendritic arms to which were attached a total of 4 or 8 molecules of Fluorol 7GA functioning as an antenna. Attachment of these additional chromophores significantly increases the spectral cross-section and overall extinction coefficient for light absorption. This should enable added cell efficiency and also the fabrication of thinner TiO₂ coatings while preserving efficient light absorption (Figure 3). In addition, the dendritic appendage was expected to decrease electron back-injection from the TiO₂ to the Ru chromophore. Figure 3 shows a schematic view of the energy transfer for a dye modified by 4 Fluorol chromophores, as well as the increase in spectral absorbance of the system; similar but more pronounced effects would be seen for the dye modified with 8 Fluorol chromophores.

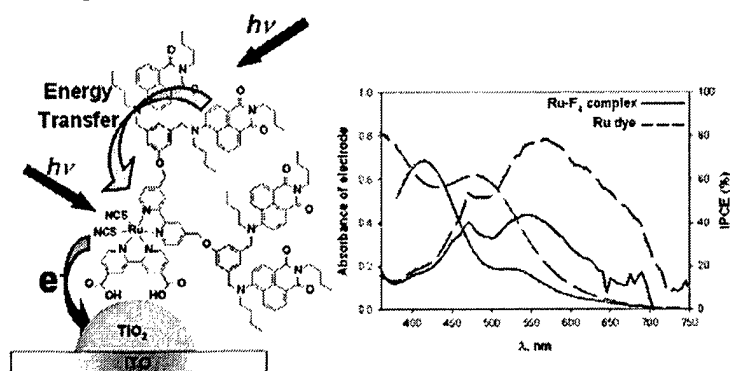


Figure 3. Energy transfer cascade in the Fluorol modified chromophores (left); spectral characteristics of the components of the modified Ru dye (right).

Once the new chromophores with Fluorol moieties attached to the Ru dye were prepared in highly purified

form, photophysical studies of the novel Ru(bpy)₃-based antenna itself showed the validity of our design as quantitative energy transfer was obtained from the Fluorol 7GA antenna to the Ru core (Figure 4). The Photophysical studies clearly demonstrate that the desired light harvesting and energy transfer goals are achieved as all energy absorbed by the Fluorol antenna is actually transferred to the Ru dye effectively doubling its efficiency. Therefore, our goal of increasing the light harvesting

capabilities of the system had been achieved, and future implementation could involve a combination of dyes for better coverage of the solar spectrum, since we had also demonstrated the concept of "cascade" energy transfer in other multichromophoric dendritic antennae [4].

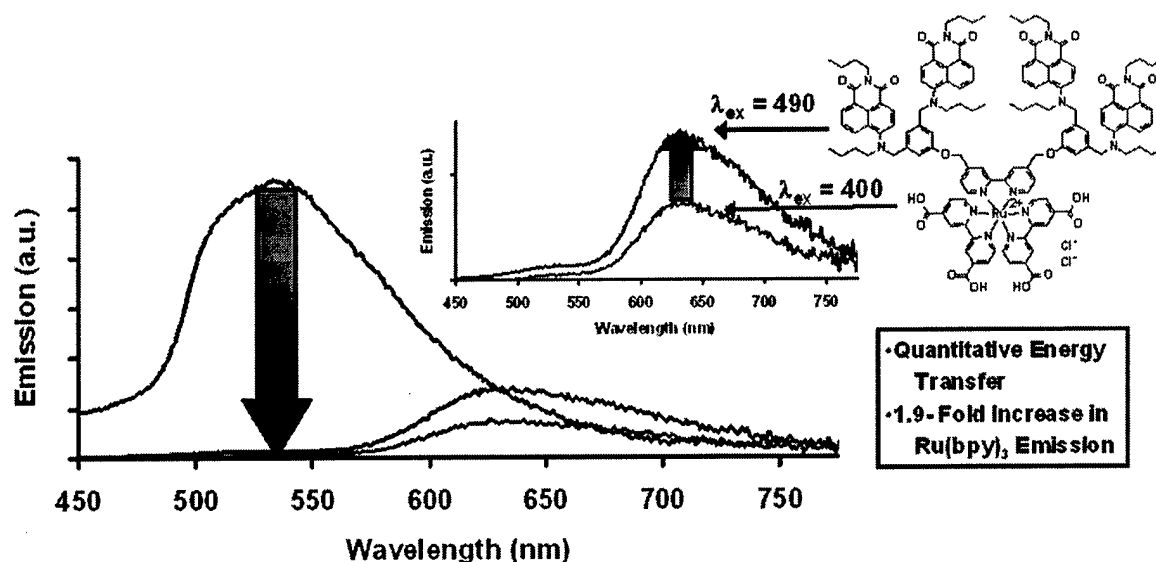


Figure 4. Demonstration of complete energy transfer from the Fluorol 7GA chromophores to the ruthenium dye with near doubling of the Ru dye emission.

The new dyes were then tested in a Grätzel cell configuration including the liquid iodine/triiodide redox electrolyte. Unfortunately, the extremely aggressive nature of the liquid electrolyte is deleterious to this system and the I_2/I_3^- electrolyte also interferes with the energy transfer process in the assembled device.

A variety of alternatives were also explored, including the use of more chemically resistant light harvesting polymers but these were unable to provide good surface coverage given the very small sizes of the pores of the Grätzel cell.

It is therefore apparent that the Grätzel cell design is not readily amenable to improvements in efficiency. Clearly the liquid electrolyte that contributes so much to the performance of the cell would have to be replaced. An issue however is the high surface area sintered nanocrystalline titania used in the cell as this material performs well with a liquid electrolyte that can penetrate even the smallest pores, but it is not ideally suited for use with polymers as they cannot penetrate small pores. Therefore a new type of cell has to be designed with:

- (i) a light absorbing electroactive polymer replacing the corrosive liquid electrolyte
- (ii) larger, more regular pores enabling full penetration and coverage of the inorganic surface by the polymer.

4) Towards hybrid polymer-inorganic photovoltaic devices.

All of our efforts in the last 18 months of this project have been directed towards the development of a hybrid polymer-inorganic photovoltaic device in which the inorganic component is responsible for electron transport and the polymer is responsible for hole transport. Light absorption can be carried out by one or both components depending on the specific choice of material. The fabrication of such hybrid photovoltaic devices can be done by solution processing on large-area flexible substrates, at modest temperatures. Hybrid photovoltaic devices can solve the issues of

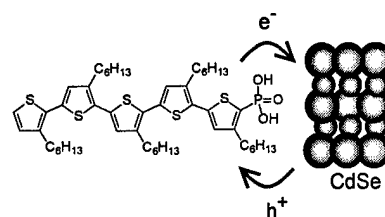
portability, flexibility, and fabrication costs associated with conventional silicon-based photovoltaics. The limiting factors for such devices are the relatively narrow spectral window of currently used materials, and, perhaps, the intrinsic low electron mobility of the organic materials. Inorganic *n*-type semiconductors typically have much higher electron mobility than organic materials. Combination of these materials with organic *p*-type semiconductors, whose hole mobility can be as high as $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (in thin-film transistor configuration) [5] can potentially improve the overall efficiency. Inorganic materials with either wide (i.e. TiO_2) or narrow (i.e. CdSe) bandgap can be used. In the former case, the organic component acts as both the sensitizer and the hole transporter, the inorganic component is only the electron transporter. In the latter case, light harvesting is shared between the components.

To demonstrate the feasibility of hybrid polymer-inorganic photovoltaic systems, we have selected polythiophenes as the electroactive polymer. Polythiophenes has many interesting attributes including its ease of synthesis, suitable bandgap, absorption characteristics and relatively high mobility. However most hybrid devices prepared with this polymer to-date have shown limited performance. We believe that this is due in large part to "electronic communications" with the inorganic material as well as issues of solubility, morphology, etc.

4.1 Polymer-Cd/Se systems

Hybrid solar cells containing CdSe nanorods and poly(3-hexylthiophene) (P3HT) were recently reported to have power conversion efficiency of 1.7% and EQE of 59 %. The high fraction of CdSe rods (90 % w/w) was said to ensure almost continuous network of *n*-type material suspended in the *p*-type polymer matrix [6]. Unfortunately these results have not been reproduced independently. The active materials in polymer/ CdSe hybrid solar cells is a composite film of CdSe nanocrystals and P3HT, prepared by cosolution blending. Integration of the nanocrystals into the cells is usually accomplished by stripping the surfactant from the nanocrystals during film processing, to achieve the direct contact between the nanocrystals and the polymer. However, when using this process, it is difficult to control the detailed morphology and dispersion of nanocrystals with the polymer. While organic surfactants such as trioctylphosphine oxide can efficiently disperse the CdSe nanocrystals within polythiophene matrix, the thick insulating monolayer of this common surfactant reduces electron transfer efficiency by a factor of at least 10. The lack of reproducibility of the performance of these cells may be in large part due to difficulties in controlling the interface between polymer and nanocrystals.

4.1.1. Electroactive surfactant approach. To enhance the interface between polymer and inorganic material, we have developed an electroactive pentathiophene surfactant containing a phosphonic acid head group that can replace the typical insulating surfactants. NMR studies showed strong binding of this functionalized oligothiophene surfactant onto the CdSe nanocrystals (see scheme), whereas mutual fluorescence quenching of pentathiophene and CdSe nanocrystals demonstrated the photoinduced charge transfer [7]. Thus the electroactive surfactant enhances the electronic communication between the inorganic material and the bulk conducting polymer. Incorporation of such surfactants into organic-inorganic heterojunction solar cells is expected to improve the efficiency of these promising devices, though our excellent findings with end-functionalized poly-thiophenes have led us to temporarily discontinue this approach.



4.1.2. End-functionalized polythiophenes. While electroactive surfactants are very promising, their synthesis, requiring multiple steps, is significantly more involved than that of linear polythiophenes. We have therefore explored the concept of directly enhancing the interaction between the polymer and the inorganic semiconductor by engineering the chain-end of the polymer. Using end-

functionalized polymer rather than a specially designed oligomeric surfactant offers a clear advantage both in terms of synthesis and also in terms of device fabrication since a simpler two-component system is feasible [8].

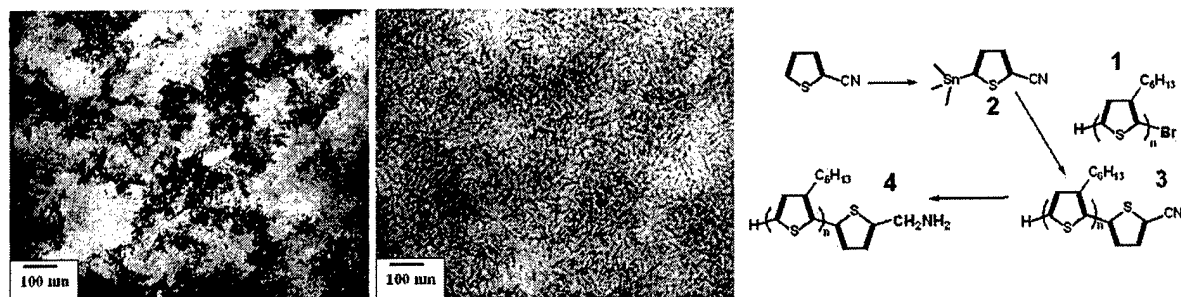


Figure 5. Preparation of end functionalized P3HT (right) and TEM images of films consisting of nanocomposites of CdSe (40 wt.%) / polymer 1 (left), and CdSe (40 wt.%) / polymer 4 (center).

As a proof of concept, we have synthesized amino-functionalized polymer surfactant 4 (Figure 5, right) and evaluated its performance in hybrid photovoltaic devices made with short CdSe nanorods. The morphology of composite films obtained using polymer 4 and using its precursor polymer 1 (without interacting end groups) was studied using transmission electron microscopy (TEM). As shown in Figure 5 (center) the films obtained with end-functional polymer 4 have a high degree of homogeneity as no aggregation of CdSe can be seen. In contrast, films prepared under the same processing conditions from a co-solution of the nanorods and polymer 1, which is the exact precursor of polymer 4, always exhibited significant phase segregation (Figure 5, left). Actual device testing carried out in multiple runs showed that the devices prepared with 4 demonstrated significant increases in power efficiency when compared to devices made using polymer 1 (P3HT), as shown in Figure 6 [8]. It is unlikely that the small end-group difference between 4 and 1 can have a significant effect on their intrinsic hole mobilities. In addition, UV/Vis analysis of the active layer films made using 4 and 1 showed essentially identical optical transmission spectra. Thus, we surmise that the enhanced performance of devices made using 4 is due to the unique morphology this functional polymer confers to the active layer.

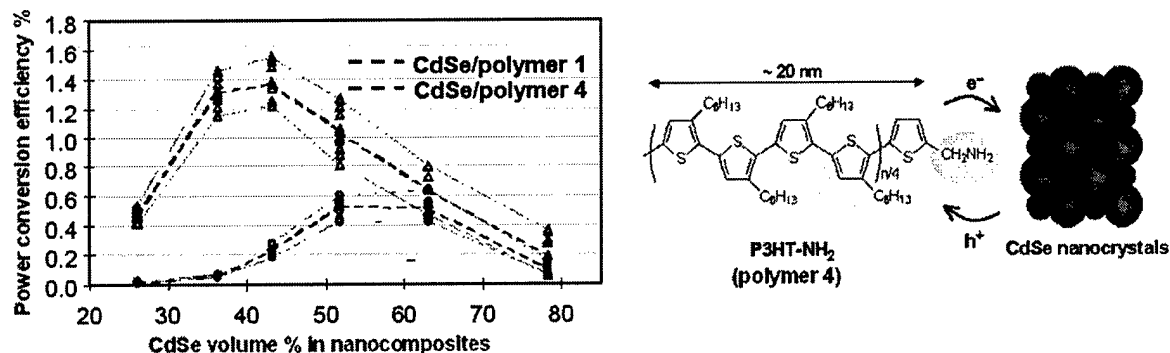


Figure 6. (Right): Interaction of end-functional P3HT with CdSe nanocrystals. (Left): Plots of power conversion efficiency (AM 1.5) versus the volume ratio of CdSe in the active layer of the devices made using polymer 4 (solid lines) and polymer 1 (dashed lines). Note the very high reproducibility of our measurements in numerous duplicate devices with lowest, highest, and average performance shown for each type of polymer.

Figure 6 also indicates that the efficiency enhancement obtained with **4** is especially substantial at lower concentrations of CdSe, which is consistent with our TEM observations. The ability to prepare more efficient solar cells using a higher proportion of polymer in the formulation (40 wt% vs. 90 wt% in earlier work) is also significant for applications involving flexible substrates.

While AFOSR funding for this project has been terminated, early results with different end-functional polymers and nanorods suggest that further significant improvements in efficiency are possible. This work is significant as it demonstrates the importance of engineering the interface between organic and inorganic components in hybrid solar cells.

4.2 Polymer-TiO₂ systems

When an unsensitized Grätzel-type TiO₂ electrode is combined with *p*-type poly(3'-undecyl-2,2'-bithiophene), efficiencies were as low or even lower than in the presence of the Ru dye, up to 0.1 % [9]. More porous TiO₂ films, melt-filled with poly(3-hexylthiophene) exhibited higher efficiencies, up to almost 0.5 % (EQE up to 15 %) [10]. One of the main reasons for this relatively low efficiency is likely to be the insufficient electronic coupling between the electroactive polymer and the titania; other reasons may include surface traps on TiO₂ surface, and various issues such as pore diameter, geometry, etc. However, titania is a very cheap and non-toxic semiconductor, and the organic polymer can be solution-processed. Thus, the TiO₂ / conducting polymer interface is extremely attractive. During the limited time available to explore this new type of hybrid photovoltaic before the termination of this grant, we focused our effort on the optimization of the titania-polymer interface and have obtained some extremely encouraging preliminary results.

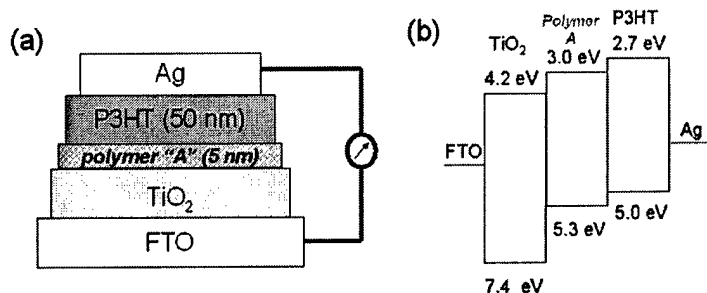


Figure 7. Device architecture (a) and energy diagram (b) of the FTO/TiO₂/polymer A/P3HT/Ag cell.

Since porous titania structures with appropriate porosities are still under development and currently do not afford reproducible results, our work has focused on planar photovoltaic

devices with the configuration shown in Figure 7a. This planar configuration is not suitable for high efficiency devices as the interface between inorganic and polymer has a very small area, but it is ideal for a fundamental study of means to optimize the electronic communication between the new electroactive polymer (designated as "A" in Figure 7) and the inorganic semiconductor. The same type of planar configuration may also be used for other inorganic semiconductors such as ZnO.

The design of polymer A is based on several considerations: (i) solubility for solution processing, (ii) presence of groups capable of interaction with the inorganic material for optimized interface, (iii) optimized energy level for enhanced electronic communications with the inorganic.

In order to make the highly conjugated organic materials solution-processable, introduction of solubilizing groups is necessary. However, typical non-conjugated solubilizing groups reduce the density of chromophores in the polymer. Therefore, it is advantageous to be able to remove these groups in a post-processing step. The thermal removal of solubilizing groups, a concept we developed more than 20 years ago with the first chemically amplified photoresist [11] and used since in several other materials such as the Durham polyacetylene, polyphenylene vinylene (PPV), for solution-processable pentacene and for organic thin film transistors (OTFTs) [12] is extremely attractive for this purpose. Using this concept, we prepared polymer "A" as shown in Figure 8. The structure of

Polymer A was selected on the basis of several considerations: (i) the tertiary nature of the ester group enables its removal at a relatively low temperature; (ii) the branched character of the ester group contributes to higher solubility, facilitating synthesis, purification, and processing; (iii) following thermal cleavage of the ester group, a carboxylic acid π -conjugated to the polymer backbone remains. This is important as such an electron-withdrawing moiety in direct conjugation with the polythiophene backbone not only allows tuning of the energy levels, but also enables the interface interaction between the polymer and TiO_2 , which can potentially enhance the interfacial charge transfer efficiency (Figure 7b). Finally, (iv) the ability to change the solubility of A through its thermal solubility switch enables the preparation of multilayer devices in which the bulk of the electroactive polymer is commercially available P3HT.

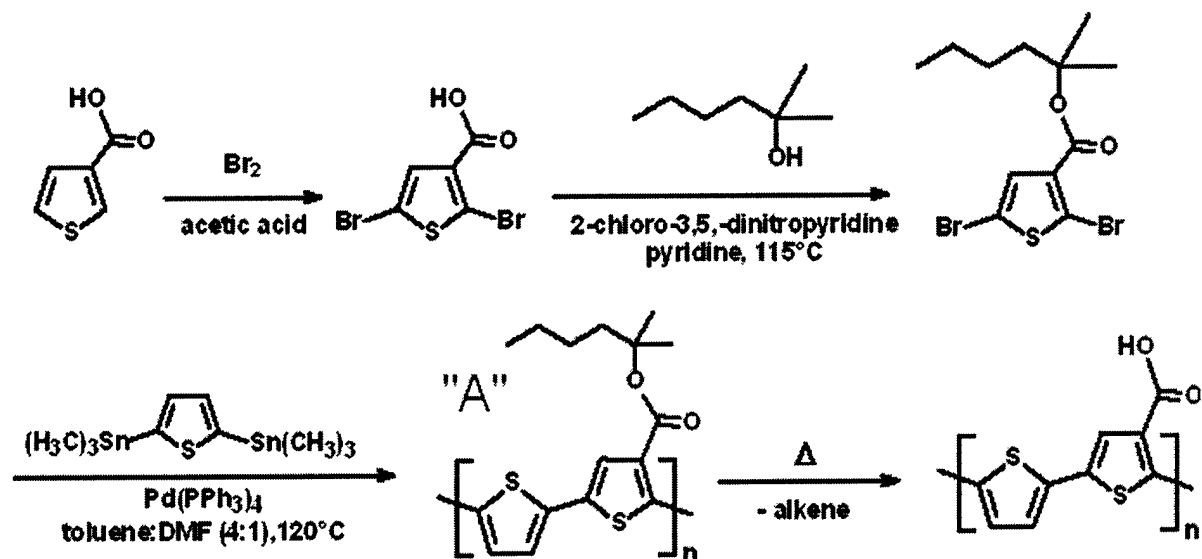


Figure 8. Synthesis of ester-functionalized polythiophene A and its thermal conversion into insoluble acid-functionalized polymer capable of interaction with TiO_2 .

As a result of this design it was expected that functionalized polythiophene A with its high chromophore density would improve the performance of polymer / TiO_2 photovoltaic cells. Thermogravimetric analysis (TGA) of A verified the expected mass loss during the thermolysis reaction. Infrared spectroscopy (IR) of polymer A before and after thermal treatment confirms the loss of ester protecting groups with appearance of carboxylic acid groups. The density of the polymer film (estimated by X-ray reflectometry), increases from 1.19 g/cm^3 to 1.44 g/cm^3 during the thermolysis step, suggesting that the thermal deprotection does not create voids in the film, but may instead contribute to an improved π - π stacking among the polymer chains.

We tested polymer A as an interface material in the very simple trilayer cell shown in Figure 7a designed to enable the careful comparison of the performance of the new functional poly(thiophene) with standard, unfunctionalized poly(3-hexylthiophene) (P3HT). A 50-nm-thick solid titania film was deposited onto glass substrates coated with fluorine-doped tin oxide (FTO). A 5-nm layer of A was spin-coated onto the titania film and heated at 210°C for 45 min to eliminate the protecting groups. As the resulting polymer film was insoluble in common organic solvents, a 50-nm layer of P3HT could then be spin-coated on top, followed by evaporation of an 80-nm silver top electrode. The trilayer device (FTO/ TiO_2 /polymer A/P3HT/Ag) was then annealed at 150°C for 4 h to improve the contact between P3HT and silver electrode. For comparison, we also made devices without polymer A

(FTO/TiO₂/P3HT/Ag). As shown in Figure 9, the device containing a layer of polymer A shows a three-fold increase in photocurrent, compared to the control without A. Under 39 mW/cm² 514-nm illumination, the FTO/TiO₂/A/P3HT/Ag cell has an external quantum efficiency (EQE) of 12.6 % and power efficiency of 1.10 %, while the control cell (FTO/TiO₂/P3HT/Ag) has an EQE of 4.2 % and power efficiency of 0.68 %.

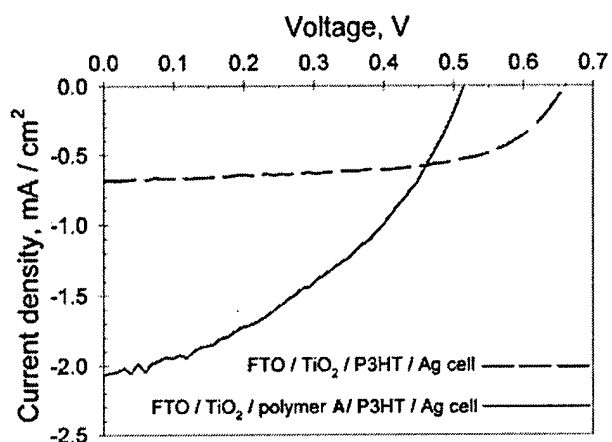


Figure 9. I-V curves of FTO/TiO₂/polymer A/P3HT/Ag cell (solid) and FTO/TiO₂/P3HT/Ag cell (dashed) under 39 mW/cm² 514-nm illumination.

We speculate that the enhancement in photocurrent may be partially attributed to the higher absorption coefficient and larger exciton diffusion length of polymer A and its carboxylic acid derivative obtained by thermolysis, compared to those parameters in P3HT. In addition, we cannot rule out the possibility that the chelation of -COOH

groups of the carboxylic acid functional derivative of A to the TiO₂ contributes to this enhancement by promoting forward interfacial electron transfer and eliminating the sub-conducting band trap sites. Although much remains to be done, it is clear that the performance enhancement obtained with the new type of interacting electroactive polymer we have developed should translate into vastly enhanced efficiencies in photovoltaic devices based on nanoporous titania or other inorganic structures with the appropriate pore geometry. We believe that the solution processable polythiophenes with removable solubilizing groups show great promise for the development of plastic solar cells as they enable both interfacial control and the tuning of electronic and optical properties.

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